

Effect of fried dishes assortment on chosen properties of post-frying soybean oils as raw material for production of engine biofuels

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Summary. The aim of the study was evaluation of effect of fried dishes assortment on quality of obtained post-frying soybean oil, with regard to its utilization as a substrate for production of engine biofuel. For the purpose of analysis of peroxide number, acid number and fatty acids composition, samples of oil after each of five heating cycles from each of three batches of oil differentiated by method of processing preceding oil sampling (frying potato chips, frying breadcrumbs coated fish fingers and heating without fried product) were taken. Purchased soybean oil and post-frying oil prepared during processing of each of above mentioned batches were subjected to esterification with methanol. Fuel obtained this way was used in engine tests.

Heating of soybean oil caused changes in the values of peroxide and acid number and fatty acid composition. These changes were depended on the method of heating oil. Utilization of esters as biocomponent of diesel fuel did not cause significant changes of investigated engine work parameters, when compared to conventional fuel. However, reduction of torque value, decrease of power and increase of specific and hourly fuel consumption were noticeable.

Key words: soybean oil, biodiesel, acid number (AN), peroxide number (PN), fatty acids composition, process of frying.

INTRODUCTION

Biofuel production of oils and fats is lately an important, principal directions of scientific research [23; 3]. An issue of special importance is a problem developing of post-frying oils and fats [20; 9; 22].

Deep-frying, method of food processing used most often in small gastronomy points, is conducted in fairly high temperature of 170–190°C, what favours processes leading to physical and chemical transformations, both in processed food products and frying medium.

Among transformations occurring in oil being frying medium, oxidation, hydrolysis, polymerization, cycliza-

tion and isomerization are considered to be the most common and the most important [18; 11; 1; 2; 4; 6; 8].

Intensity and type of transformations occurring in particular system are often determined by numerous present in it factors, among which [8] list as basic the following ones: conditions of carrying out the process (its duration, temperature and periodicity) and degree of unsaturation of fatty acids in triglycerides of fat. Among factors shaping properties of frying medium also oxygen availability and amount and composition of compounds released from food (e.g. pro and antioxidants and presence of water) are listed [8].

Numerous transformations occurring in frying medium may be side effect of deep-frying. They are often precursors of synthesis of many various compounds of often complex, and not always determined structure. Products of these transformations can be usually classified in one of two categories: volatile compounds (hydrocarbons, fatty acids and carboxylic compounds) or non-volatile (monomers, dimers, polymers and also some aldehydes and ketones, as well as fatty acids characterizing with changed melting point) [18].

Water transferred into frying environment usually originates from fried products or can be a remain of process of maintenance and cleaning of frying equipment. When present in fat, it is a base for multi-directional hydrolytic transformations, contributing this way to increase of acid number (AN). Moreover, presence of water favours heat transport and stabilization of food frying temperature. At the same time, water vapour partly inhibits oxidation transformations of fat by displacing oxygen in it [8].

Loss of water occurring in fried product is often balanced by sorption of frying fat surrounding fried product. It is a dynamic balance determining process of frying, and shaping properties of product. As a result of these two opposing processes (vaporization and sorp-

tion of frying medium) fried product is „enriched” with post-frying oil, which content, dependent on type of fried product and parameters of process, ranges significantly reaching even approx. 40% [8].

High capacity of fryers favours formation of layers of oil, which are more distant from fried product and hence contain less oxygen and water vapour. Above mentioned factors favour mainly polymerization and free-radical transformations of unsaturated fatty acids. The most common result of these transformations are numerous, having complex structure, nonpolar thermal polymers. Macroscopic result of this type of reactions is increase of viscosity and darkening as well as increase of melting point of frying medium, what results in change of its state of aggregation. It results with precipitation of dark brown deposits found on walls of a fryer, which can be a reason for many problems related to utilization of such oil [6].

Searching for alternative energy sources has resulted, in recent years, the development of research on new technologies for production of biofuels from various sources. [5, 10]. However, studies on the use of post-frying vegetable oils as a raw material in biofuels production [9, 20, 12] represent an important new direction of economic and ecological management of the onerous waste produced in a small gastronomy.

THE AIM OF STUDY

Goal of this research was comparison of physicochemical changes taking place in soybean oil subjected to cyclic heating without fried product with changes caused by heating in process of five-time cyclic frying of potato chips or breadcrumbs coated fish fingers.

Aim of the research was evaluation of effect of fried dishes assortment on quality of obtained post-frying soybean oil, with regard to its utilization as a substrate for production of engine biofuel.

MATERIALS AND METHODS

In this research soybean oil purchased in a shop was used as frying medium, and for the purpose of this investigation was called raw soybean oil.

Preparation of Post-frying Soybean Oils. From total amount of raw oil, sample for laboratory analyses was taken. It was marked as „0”. Remaining amount of oil was divided into three batches and poured into separate containers. First part of oil was heated to temperature of 180°C, which has been maintained for 10 min. Oil was left in the container to cool down to room temperature and than sample for laboratory tests was taken. It was marked as „heating I -without fried product”. Second batch of oil was also heated to 180°C, and than potato chips, prepared of purchased raw potatoes and cut to the size and shape of frozen potato chips found in trade, were fried. After frying and separating chips, oil was cooled down to room temperature and than sample for research

was taken. It was marked as „heating I - process of chips frying”. Third part of oil (batch no. 3) was heated same way as batch no. 1 and no. 2 but in this case, purchased breadcrumbs coated fish fingers were the fried product. After frying and separating breadcrumbs coated fish fingers, oil was cooled down to room temperature and than sample for research was taken. It was marked as „heating I - process of breadcrumbs coated fish fingers frying”.

In consecutive stage of the investigation, after 24 hours, remaining 3 batches were heated again and all described above actions were repeated – yielding another laboratory sample marked as heating II. Whole process of heating, cooling and sampling oil fraction was repeated until it yielded samples marked with numbers III, IV and V.

Chemical Analysis. Each of collected samples was subjected to laboratory tests of peroxide number (PN) [14], acid number (AN) [15] and composition of higher fatty acids [6]. Determination of higher fatty acids composition was conducted by means of method based on utilization of gas chromatography. In this method sample of fat is subjected to alkaline hydrolysis in anhydrous environment with utilization of methanol solution of sodium hydroxide, and mixture of sodium soaps of higher fatty acids of investigated oil is obtained. The mixture is than subjected to reaction of esterification with anhydrous solution of hydrogen chloride in methanol, yielding mixture of fatty acids methyl esters. Obtained methyl esters are separated in a chromatographic column and than their participation in a sum of fatty acids is determined [6]. Chromatographic separation was conducted by means of gas chromatograph with nitrogen as carrier gas, packed column (2.5 m with stationary phase PEGA - polyethylene glycol adipate on carrier GAZ-CHROM-Q and flame ionization detector).

Methyl Esters Preparation. Samples of soybean oil which remained after laboratory samples had been taken from each of three batches, differentiated by type of initial preparation (frying potato chips, frying bread-crumbs coated fish fingers and heating without fried product) were separately subjected to esterification with methanol. They were obtained by method analogous to one used in investigation of fatty acids composition by means of gas chromatography [6]. Fuel obtained this way was used in engine tests including main engine work parameters.

Biofuels Mixtures. Four mixtures were prepared, each containing 90% diesel fuel and 10% addition of higher fatty acids methyl esters obtained in research and marked as:

- 1) M1 - esters obtained from purchased fresh soybean oil,
- 2) M2 - esters obtained from soybean oil subjected to five-time cyclic heating without addition of fried product,
- 3) M3 -esters obtained from soybean oil, previously used for five-time cyclic frying of potato chips,
- 4) M4 -esters obtained from soybean oil, previously used for five-time cyclic frying of breadcrumbs coated fish fingers.

As reference engine was powered with diesel fuel (DF).

Engine Tests. Above mentioned fuel mixtures, were used for powering 2CA90 diesel engine installed on dynamometric stand for purpose of conducting measurements of its energetic work parameters. Test bed comprised of following devices:

- internal combustion diesel engine 2CA90,
- dynamometric stand composed of eddy-current brake AMX210 and control-measurement system AMX201, AMX 211,
- fuel consumption measuring system,
- system measuring engine parameters: exhaust gasses temperature - tsp, engine oil temperature - tol, oil pressure - pol,
- system measuring state of environment: temperature of environment - tot, atmospheric pressure - pa, and air humidity - φ.

Measurements for each of investigated fuels were conducted and obtained results of energetic parameters were elaborated. Data yielded by measurements was used to draw external characteristics of the engine for rotational speed ranging from minimal to nominal. Carried out research included kinematic and dynamic parameters of the engine: torque - Mo, rotational speed - n, time in which set amount of investigated fuel was used - τ. Amount of fuel used for purpose of this characteristic was 50 g. Methodology of measurements and methods of measurements and results reduction of power and torque, were in conformity with norms [13; 17].

RESULTS AND DISCUSSIONS

Chemical analysis. Raw soybean oil characterised with typical properties for edible oils, fulfilling requirements of recommended in Poland Norm [17], with regard to peroxide number (PN), acid number (AN) as well as composition of higher fatty acids.

Heating soybean oil caused significant decrease of its quality. Peroxide number (PN) of heated samples was significantly increased. It must be noted that diverse course and intensity of these changes were observed in case of samples heated without product, samples heated in process of potato chips and breadcrumbs coated fish fingers frying.

Peroxide number of samples heated in process of potato chips frying, for each of five heating cycles, remained at lower level than in samples of oil heated without fried products. Stabilizing effect of potato chips, caused by sorption of oxidation products on their surface or partial absorption of frying fat, might be explanation of such phenomenon. Similar results were obtained in earlier research concerning rapeseed oil [20] and oil heated in process of potato chips frying [20], had similar course stabilizing at approx. 2 mmol/100g and approx. 1.5 mmol/100g respectively (with exemption of null samples and first cycle of soybean oil heating). Samples of soybean oil and rapeseed oil heated without fried product, differed

significantly - reaching almost two times higher value of peroxide number (PN) than respective samples heated in process of potato chips frying. While heating sunflower oil in process of potato chips frying caused only slight decrease of its peroxide number (PN) when compared to samples heated without fried product [9]. Frying breadcrumbs coated fish fingers caused initial, after first and second heating cycle, fast increase of peroxide number of soybean oil, what can probably be related to introduction of fat present in fried product, which was followed by stabilization of peroxide number level, analogous to stabilization observed in process of potato chips frying (Figure 1).

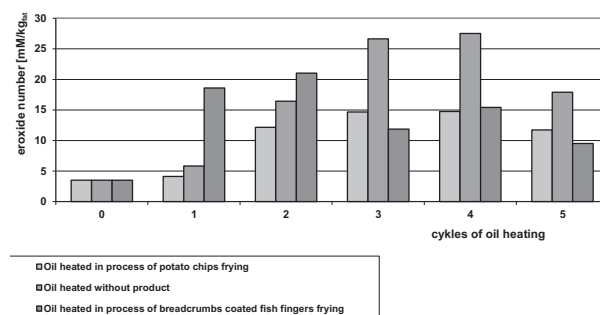


Fig. 1. Course of peroxide number (PN) changes during subsequent cycles of soybean oil heating

Acid number (AN) of heated oil samples, was higher than AN observed in samples of raw oil. However, heating in process of potato chips frying caused stabilization of acid number value (AN) at similar level (0.02 mg KOH/g) regardless of number of oil heating cycles, while heating without the product caused systematic increase of AN. Similar course of acid number changes of investigated post-frying oils was also observed in analogous research on rapeseed oil [20] and sunflower oil samples [9]. Probable cause of observed changes of acid number of these samples is sorption of oxidation products on surface of, subjected to culinary processing, potato chips, or partial absorption of oil surrounding product into its deeper, more distant from surface of investigated raw product, layers.

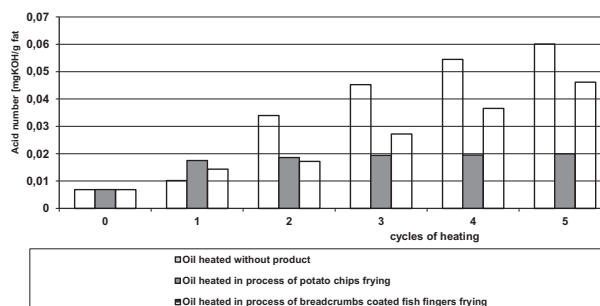


Fig. 2. Course of acid number (AN) changes during subsequent cycles of soybean oil heating

Heating soybean oil in process of breles, reaching values lower than in respective samples of soybean oil heated without fried product (Figure 2). Two opposing processes were the most probable cause of above described course

of changes of acid number (AN) in samples of soybean oil heated in process of breadcrumbs coated fish fingers frying. Increase of AN should be explained with oxidation of higher fatty acids and hydrolytic effect of water and water vapour, released from product as a result of frying, while stabilization of its level occurred as an effect of sorption of oxidation products in surface layer of fried product.

It should be noted that composition of higher fatty acids of raw soybean oil was $_{40}$ typical for this product. Properties of this $_{30}$ oil are determined mainly by three unsaturated fatty acids (linolenic, oleic and linoleic), proportion of content of which in raw oil is 1:4.3:8.8 (Figure 3). Both, heating without fried product as well as process of breadcrumbs coated fish finificant changes of soybean oil properties. These changes are mainly result of significant decrease of oil higher fatty acids content and significant increase of oxidation products content (Figure 3-5), what was confirmed by earlier research on this problem conducted on samples of rapeseed [20] and sunflower oil [9].

Frying breadcrumbs coated fish fingers or potato chips caused partial stabilization of higher fatty acids composition, what can be noted in case of two, dominating in soybean, fatty acids i.e. oleic and linoleic. Their content in typical raw soybean oil often exceeds 75% (Figure 3-5), [19; 21]. Five-time cyclic heating of soybean oil only slightly changed proportion of oleic to linoleic acid, for in raw oil, on one particle of oleic acid statistically slightly more than two particles of linoleic acid are found. After process of heating, this rate is approx. 1:1.5, from 1:1.4 for sample heated without fried product, through 1:1.50 for sample heated in the process of frying potato chips, and up to 1:1.63 when sample of oil heated in the process of frying breadcrumbs coated fish fingers was investigated.

The same processes of heating caused also slight changes of saturated fatty acids ratio. In fresh soybean oil, on one particle of stearic acid 2.66 particles of palmitic acid are found, while after five cycles of heating this ratio was from 1:2.1 in oil heated without product (Figure 3), through 1:2.31 in oil subjected to heating in process of potato chips frying (Figure 5) to 1:2.38 in oil subjected to heating in process of breadcrumbs coated fish fingers frying (Figure 4).

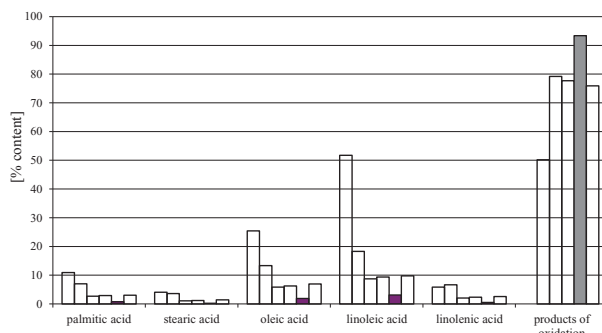


Fig. 3. Composition of higher fatty acids of soybean oil subjected to five-time cyclic heating without fried product AN for first two cycles of heating remained at level siver, starting from the third heating cycle 90 AN exceeded this value and was systema⁻⁸⁰

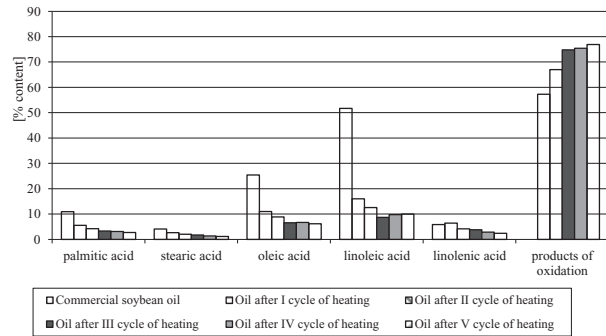


Fig. 4. Composition of higher fatty acids of soybean oil subjected to five-time cyclic heating in process of breadcrumbs coated fish fingers frying

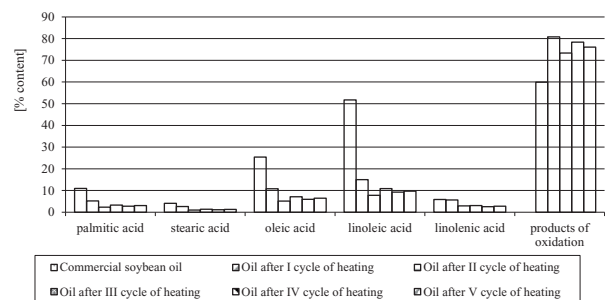


Fig. 5. Composition of higher fatty acids of soybean oil subjected to five-time cyclic heating in process of potato chips frying

Cyclic five-time heating of soybean oil contributed to occurrence of clear change i.e. increase of linolenic acid content in proportion to unsaturated fatty acids. After five cycles of heating, on one particle of linolenic acid from 2.34 to 2.69 particles of oleic acid, and from 3.50 to 4.14 particles of linoleic acid were found (Figure 3, 4, 5), while in raw oil respective values were 4.3 and 8.8.

Utilization of post-frying soybean oil for production of components of higher fatty acids esters as engine biofuels seems to be hindered mainly by elevated acidity of raw material and significant content of oxidation products of higher fatty acids, which could not be identified by means of chromatography. However, up to date research on utilization of post-frying rapeseed oil has not confirmed these doubts [12].

In conclusions, being summary of this research, authors indicate fact that elevated acidity of post-frying oils is neutralized during stage of alkaline hydrolysis, which is an essential phase of transforming oil into fatty acids methyl esters. Unidentified oxidation products undergo similar transformations in the process of fatty acids methyl esters formation, and are not a significant obstacle in correct operation of diesel engines powered with such type of biofuel [12]. Stabilizing effect of fried product, e.g. potato chips [20], on proportion of higher fatty acids of post-frying oil is also emphasized.

Engine Tests. Presented current engine tests seem to confirm previously observed patterns [12]. Utilization of mixtures of diesel fuel and 10% addition of fatty acids methyl esters derived from purchased raw soybean oil and

post-frying oils, obtained after five-time cyclic heating without fried product and after five-time cyclic frying of potato chips or breadcrumbs coated fish fingers, lead to decrease of power of engine powered with these mixtures, when compared to conventional diesel fuel (Figure 6). Similarly as in previously mentioned research [12], course of curves of engine power in relation to its rotational speed showed similar course and character. Differences in course of changes of these curves (Figure 6) for above mentioned mixtures containing 10% addition of esters, are similar and all of them have similar effect on changes of power of investigated engine in relation to its these changes course, regardless of utilized fuel mixtures rotational speed. (Figure 7). These results are also confirmed by prior research [12].

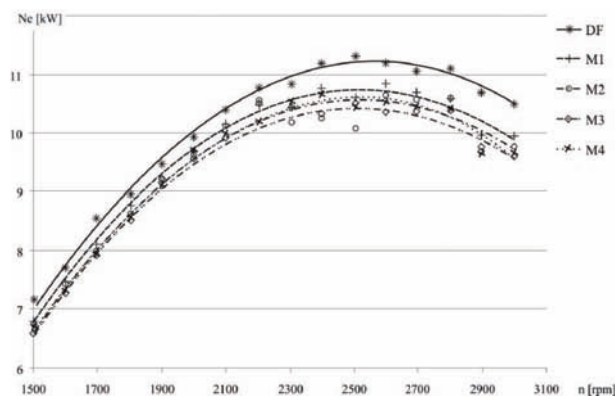


Fig. 6. Course of power changes of 2CA90 engine powered with diesel fuel and mixtures of fatty acids methyl esters and diesel fuel: a) M1 - esters obtained from purchased fresh soybean oil, b) M2 - esters obtained from soybean oil subjected to five-time cyclic heating without addition of fried product, c) M3 - esters obtained from soybean oil, previously used for five-time cyclic frying of potato chips, d) M4 - esters obtained from soybean oil, previously used for five-time cyclic frying of breadcrumbs coated fish fingers, e) DF - diesel fuel

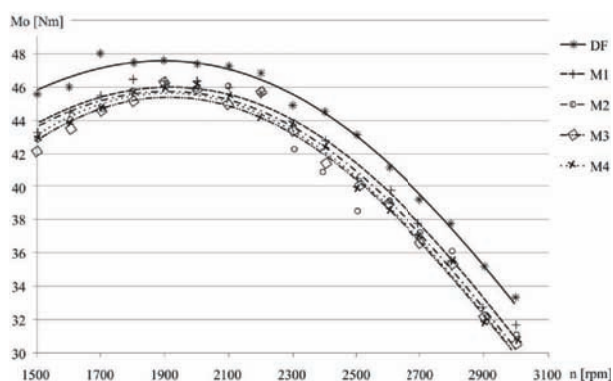


Fig. 7. Course of torque changes of 2CA90 engine powered with diesel fuel and mixtures of fatty acids methyl esters and diesel fuel: a) M1 - esters obtained from purchased fresh soybean oil, b) M2 - esters obtained from soybean oil subjected to five-time cyclic heating without addition of fried product, c) M3 - esters obtained from soybean oil, previously used for five-time cyclic frying of potato chips, d) M4 - esters obtained from soybean oil, previously used for five-time cyclic frying of breadcrumbs coated fish fingers, e) DF - diesel fuel

Approximation of research data, including investigation of course of 2CA90 engine torque changes in relasts on 2CA90 engine, demonstrate significantly lower consumption of fuel when conventional diesel fuel is used. Curves of fuel consumption for investigated fuel mixtures, when compared with results for DF, characterize with higher values at each of investigated rotational speeds. At the same time they all have similar character and considerable similarity of course. It suggests insignificance of differences between them. Similar results were obtained in previous research [12].

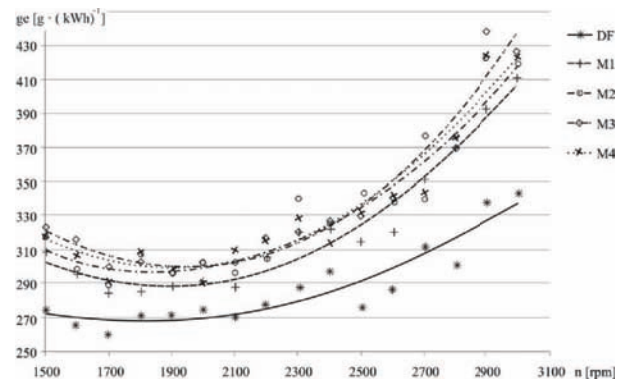


Fig. 8. Course of specific fuel consumption changes of 2CA90 engine powered with diesel fuel and mixtures of fatty acids methyl esters and diesel fuel: a) M1 - esters obtained from purchased fresh soybean oil, b) M2 - esters obtained from soybean oil subjected to five-time cyclic heating without addition of fried product, c) M3 - esters obtained from soybean oil, previously used for five-time cyclic frying of potato chips, d) M4 - esters obtained from soybean oil, previously used for five-time cyclic frying of breadcrumbs coated fish fingers, e) DF - diesel fuel

CONCLUSIONS

Relying on results of carried out investigation following conclusions can be formulated:

1. Cyclic, model heating of soybean oil, and especially three first cycles, contribute to significant changes in composition of higher fatty acids. It results with decrease of unsaturated fatty acids content, significant increase of oxidation products content and changes of peroxide number (PN) and acid number (AN) of heated oil.
2. Heating soybean oil in process of frying products like breadcrumbs coated fish fingers or potato chips affects stabilization of amount of peroxide products present in post-frying oil, what leads to decrease of peroxide number (PN) of such oil in comparison to process of heating without fried products.
3. Acid number (AN) of post-frying soybean oil obtained after frying potato chips stabilizes, while frying breadcrumbs coated fish fingers and heating oil without fried product contribute to gradual increase of AN.
4. Frying breadcrumbs coated fish fingers and potato chips favour stabilisation of proportion of oleic and

- linolic acid in investigated post-frying oil, at level similar to one noted in case of purchased raw soybean oil.
- Unification of properties of post-frying soybean oil occurring during stage of chemical conversion to fatty acids methyl esters, contributes to unification of properties of biofuels prepared on base of various batches of post-frying oil and favours utilization of post-frying oils which proved as suitable for production of biofuel components as fresh soybean oil.

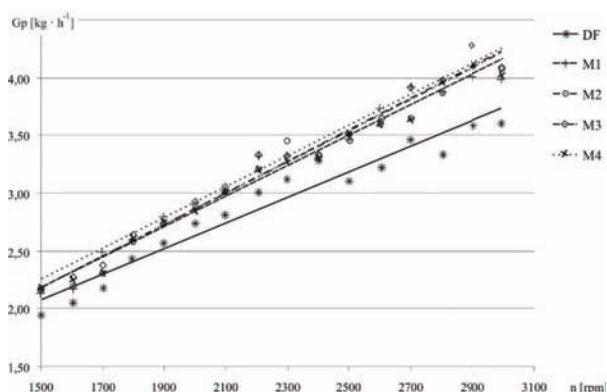


Fig. 9. Hourly fuel consumption of 2CA90 engine powered with diesel fuel and mixtures of fatty acids methyl esters and diesel fuel: a) M1 - esters obtained from purchased fresh soybean oil, b) M2 - esters obtained from soybean oil subjected to five-time cyclic heating without addition of fried product, c) M3 - esters obtained from soybean oil, previously used for five-time cyclic frying of potato chips d) M4 - esters obtained from soybean oil, previously used for five-time cyclic frying of breadcrumbs coated fish fingers, e) DF - diesel fuel

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EFFECT OF FRIED DISHES ASSORTMENT ON CHOSEN PROPERTIES OF POST-FRYING SOYBEAN OILS AS RAW MATERIAL FOR PRODUCTION OF ENGINE BIOFUELS [PO POLSKU]

Streszczenie. Celem pracy była ocena wpływu asortymentu dań smażonych na jakość otrzymanego po smażeniu oleju sojowego, w odniesieniu do jego wykorzystania jako

bazy dla produkcji biopaliwa do silników. Dla celów analizy liczby nadtlenkowej, ilości kwasów i kwasów tłuszczowych, pobrano próbki oleju po każdym z pięciu cykli ogrzewania z każdego z trzech partii oleju zróżnicowanego w zależności od metody przetwarzania (po smażeniu frytek, paluszków rybnych powlekanych bułką tartą i po ogrzewaniu bez smażonego produktu). Zakupiony olej sojowy oraz olej po smażeniu podczas przetwarzania każdej z wyżej wymienionych partii poddano estryfikacji metanolem. Paliwo uzyskane w ten sposób było używane w testach silnikowych. Ogrzewanie oleju sojowego powodowało zmiany wartości liczby nadtlenkowej i kwasowej

i składu kwasów tłuszczowych. Zmiany te były uzależnione od sposobu ogrzewania oleju.

Wykorzystanie estrów jako biokomponentu oleju napędowego nie spowodowało istotnych zmian parametrów pracy badanego silnika, w porównaniu z konwencjonalnym paliwem. Jednakże zauważono obniżenie wartości momentu obrotowego, zmniejszenie mocy i wzrost całkowitego oraz godzinowego zużycia paliwa.

Słowa kluczowe: olej sojowy, biodiesel, liczba kwasowa (AN), liczba nadtlenkowa (PN), skład kwasów tłuszczowych, proces smażenia.